# In Situ Chemical Oxidation: Design & Implementation

**October 30, 2002**
NJDEP Public Hearing Room
Sponsors:  NJDEP & ITRC

1:00 - 1:15 **Welcome**

**Brian Sogorka,** NJDEP Remediation Technology Manager

1:15 - 1:25 **ITRC Update**

**Marybeth Brenner,** NJDEP

1:25 - 2:10 **Available Oxidants and Oxidant Selection**

**Kenneth L. Sperry,  P.E., XPERT DESIGN & DIAGNOSTICS, LLC**

2:10 - 2:55 **Laboratory and Field Pilot Test Design**

**Dr. John Cookson**, **XPERT DESIGN & DIAGNOSTICS, LLC**

2:55 - 3:40 **Full-Scale Design and Implementation**

**Kenneth L. Sperry, P.E. and Dr. John Cookson,**
**XPERT DESIGN & DIAGNOSTICS, LLC**

3:40 - 3:45 Wrap-up

# In Situ Chemical Oxidation

INTERSTATE TECHNOLOGY REGULATORY COUNCIL

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## Purpose of ITRC

ITRC is a state-led, national coalition of regulators and others working to

* improve state permitting processes and
* speed implementation of new environmental technologies.

ACCEPTANCE

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## Introduction:

**Brian Sogorka,**
NJDEP Remediation Technology Manager

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## Goals

* Achieve better environmental protection through innovative technologies
* Reduce the technical/regulatory barriers to the use of new environmental technologies
* Build confidence about using new technologies

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## Regulatory Acceptance for New Solutions

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ITRC Point of Contact
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## Other Participants

• Industry representatives
• Academia
• Public stakeholders
• Federal agencies

U.S. Department of Energy

U.S. Environmental Protection Agency

U.S. Department of Defense

• Host organization

Environmental Council of the States
ECOS

• State organizations

Western Governors' Association

Southern States Energy Board

## Products & Services

* Regulatory and Technical Guidelines
* Technology Overviews
* Case Studies
* Peer Exchange
* Technology Advocates
* Classroom Training Courses
* Internet-Based Training Sessions

## Contacts

Web Site: http://www.itrcweb.org

### Cochairs, ITRC Board of Directors:

Brian C. Griffin  Oklahoma Secretary of Environment
(405) 530-8995  bcgriffin@owrb.state.ok.us

Ken Taylor  SC Department of Health and
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taylorgk@dhec.state.sc.us

### Program Director:

Rick Tomlinson  rickt@sso.org
(202) 624-3669

## Active Technical Teams

* Alternative Landfill Technologies
* Brownfields
* Constructed Wetlands
* Contaminated Sediments
* Dense Nonaqueous Phase Liquids
* Diffusion Samplers
* DOE Gate 6 Technologies
* In Situ Bioremediation

- MTBE-Contaminated Groundwater
- Permeable Reactive Barriers
- Radionuclides
- Remedial Process Optimization
- Sampling, Characterization, and Monitoring
- Small Arms Firing Range
- Unexploded Ordnance

## Technical Program

NJDEP, Moderator

**Available Oxidants and Oxidant Selection**
Kenneth L. Sperry, P.E.,
XPERT DESIGN & DIAGNOSTICS, LLC

**Laboratory and Field Pilot Test Design**
Dr. John Cookson
XPERT DESIGN & DIAGNOSTICS, LLC

**Full-Scale Design and Implementation**
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## Nationwide Success

## Slide 1

In Situ Chemical Oxidation:
Design & Implementation

October 30, 2002
NJDEP Public Hearing Room
Sponsors: NJDEP & ITRC



## Slide 2

*Presented by*

Kenneth L. Sperry, P.E.
John Cookson, Jr., Ph.D.

**X**PERT **D**ESIGN and **D**IAGNOSTICS, LLC
22 Marin Way, Stratham, NH
www.XDD-LLC.com

## Slide 3

**Available Oxidants**



## Slide 4

**Available Oxidants**

| Oxidant | Potential (V) | Form | Cost/ equiv |
|---|---|---|---|
| Fenton's Reagent (OH•) | 2.8 | Liquid | |
| Perozone ($O_3$ + Peroxide) | 2.8 | Gas/Liquid | |
| Activated Persulfate ($SO_4^-$•) | 2.6 | Salt Liquid | — |
| Ozone ($O_3$) | 2.42 2.07 | Gas | 0.020 0.053 |
| Persulfate ($S_2O_8^{2-}$) | 2.01 | Salt Liquid | 0.030 |
| Hydrogen Peroxide ($H_2O_2$) | 1.78 | Liquid | 0.026 |
| Permanganate ($MnO_4^-$) | 1.68 | Salt Liquid | 0.017 - K 0.031 - Na |

Costs adapted from Siegrist et al., 2001

## Slide 5

**Permanganate – $MnO_4^-$**

• **$KMnO_4$ Salt**

• **$NaMnO_4$ Solution (40%)**

Source: XDD, LLC

**Direct Oxidation**

$$MnO_4^- + 4H^+ + 3e^- ® MnO_{2(s)} + 2H_2O$$

## Slide 6

**Permanganate – $MnO_4^-$**

• **Used in waste water treatment for decades**
• **Used in organic chemical manufacturing**
• **Application for in-situ remediation was first recognized by Farquhar at U of Waterloo, 1989**
• **Mined from ore and therefore has other constituents or impurities**
• **Supplied in grades based on purity and flow properties**

Source: XDD, LLC

## Permanganate – $MnO_4^-$

| Advantages | Disadvantages |
|---|---|
| • High stability in subsurface<br> • Provides better overall efficiency<br> • Allows for diffusion into tight soils & porous rock<br>• No gas/heat production - less health & safety issues<br>• Applicable over wide pH range<br>• Many successful in-situ field applications | • Lower oxidation potential \ Narrower range of contaminant applicability<br>• Metal impurities in product*<br>• Potential pore clogging due to precipitates* |

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## Persulfate – $S_2O_8^{2-}$

- $Na_2S_2O_8$ Salt
- $Na_2S_2O_8$ Solution
- Can also form free radicals through heat or transitional metals

**Direct Oxidation**

$$S_2O_8^{2-} + 2e^- \circledR 2SO_4^{2-}$$

**Free Radical Formation**

$$S_2O_8^{2-} + 2Fe^{+2} \text{ (or Heat)} \circledR 2SO_4^{-\bullet} + 2Fe^{3+}$$

**S** Sulfur
Atomic Number: 16
Atomic Mass: 32.06

**O** Oxygen
Atomic Number: 8
Atomic Mass: 16

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## Persulfate – $S_2O_8^{2-}$

- Used in polymerization and organic chemical manufacturing
- Used in pulp and paper industry
- Used in electronics as an etchant
- Used as soil stabilizer
- Recently being used for in-situ chemical oxidation

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## Persulfate – $S_2O_8^{2-}$

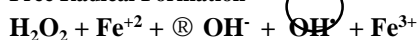| Advantages | Disadvantages |
|---|---|
| • Can be catalyzed by reduced metals or heat to promotes Sulfate Free Radical (SFR) formation<br>• High oxidation potential \ applicable to wide range of organics<br>• Can be combined with permanganate (DUOX) | • Relatively new technology and limited field pilot studies<br>• Catalyst required for activated persulfate system are currently under development |

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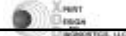
## Hydrogen Peroxide – $H_2O_2$

- $H_2O_2$ solution
- Can also form free radicals through activation with transitional metals

**Direct Oxidation**
$$H_2O_2 + H^+ + e^- \circledR OH^- + H_2O$$

**Free Radical Formation**
$$H_2O_2 + Fe^{+2} + \circledR OH^- + OH^{\bullet} + Fe^{3+}$$

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## Hydrogen Peroxide – $H_2O_2$

- Many industrial applications
  - Effluent treatment
  - Electrical manufacturing
  - Food manufacturing
  - Pulp and Paper

- Used for in-situ remediation since 70's

# Hydrogen Peroxide – $H_2O_2$

### Advantages

- High oxidation potential \ applicable to wide range of organics
- The most studied of the oxidizing compounds for remediation
- Can be combined with ozone (perozone)

### Disadvantages

- Reaction's gas/heat production – health & safety hazard
- Short half-life \ limited travel distances, requires closely spaced injection points
- Optimal pH between 3–5
- Ineffective in alkaline environments

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# Ozone – $O_3$

- Only available as a gas
- Degrades to dissolved oxygen
- Reacts with water or peroxide to produce hydroxyl-radicals
  - Direct Oxidation Under Acidic pH's

$$O_3 + 2H^+ + 2e^- \to O_2 + 2H_2O$$

  - Free Radical Formation

$$O_3 + OH^- \to O_2^- + HO_2^\bullet$$

  - Criegee Oxidation (Nucleophillic Substitution)

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# Ozone – $O_3$

- Used in many processes:
  - Wastewater treatment
  - Industrial effluent treatment
  - Aquaculture
  - Bleaching
  - Drinking water
- Generated on-site due to limited stability
- Made from air or oxygen

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# Ozone – $O_3$

### Advantages

- High oxidation potential \ applicable to wide range of organics
- Easier to apply than liquid oxidants in vadose zone
- Generated on-site, allows for continual application
- Decomposes to oxygen which can stimulate aerobic biodegradation

### Disadvantages

- Highly unstable - short half-life
- Effective distribution in saturated zone requires closely spaced injection points
- Confined aquifer usage requires pressure (gas) relief

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# Oxidant Selection

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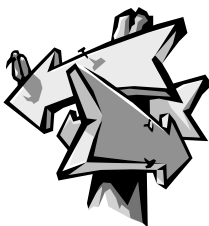
# Contaminant Type

| Contaminant | $MnO_4$ | $S_2O_8$ | $SO_4^\bullet$ | Fenton's | Ozone |
|---|---|---|---|---|---|
| Petroleum Hydrocarbon | G | G/E | E | E | E |
| Benzene | P | G | G/E | E | E |
| Phenols | G | P/G | G/E | E | E[1] |
| Polycyclic Aromatic Hydrocarbons (PAHs) | G | G | E | E | E |
| MTBE | G | P/G | E | G | G |
| Chlorinated Ethenes (PCE, TCE, DCE, VC) | E | G | E | E | E |
| Carbon Tetrachloride | P | P | P/G | P/G | P/G |
| Chlorinated Ethanes (TCA, DCA) | P | P | G/E | G/E | G |
| Polychlorinated Biphenyl's (PCBs) | P | P | P | P | G[1] |
| Energetics (RDX, HMX) | E | G | E | E | E |

P = poor   G = good   E = excellent   1=Perozone

# Contaminant Distribution

**Factors Affecting Selection:**

1. Source Zone Treatment

2. Poorly defined or large areas of low concentrations (dissolved plumes)
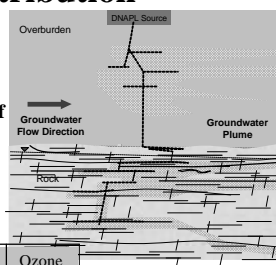


| Criteria | $MnO_4$ | $S_2O_8$ | Fenton's | $SO_4\bullet$ | Ozone |
|---|---|---|---|---|---|
| 1 | E | E | E | E | E |
| 2 | P/G | P/G | P | P | P/G |

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# Geologic Considerations

**Unconsolidated Materials:**

1. Higher permeability sands to gravels
   - Advection dominated
2. Lower permeability silts to clays
   - Diffusion dominated
3. Combinations of lower and higher permeability zones
   - Advection and diffusion dominated



Nelson, 1999

| Criteria | $MnO_4$ | $S_2O_8$ | Fenton's | $SO_4\bullet$ | Ozone |
|---|---|---|---|---|---|
| 1 | E | E | E | E | E |
| 2 | G | G | P | P | P |
| 3 | G/E | G/E | P | P | P |

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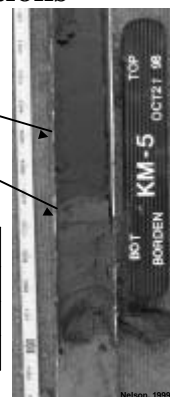
# Geologic Considerations

**Consolidated Materials:**

1. Secondary porosity features (fractures, parting planes, etc.)
   - Advection dominated
2. Primary porosity features
   - Diffusion dominated

| Criteria | $MnO_4$ | $S_2O_8$ | Fenton's | $SO_4\bullet$ | Ozone |
|---|---|---|---|---|---|
| 1 | E | E | P/G | P/G | P/G |
| 2 | G | G | P | P | P |

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# Hydrogeologic Considerations

**Factors that Influence Oxidant Selection Include:**

1. Saturated zone
2. Unsaturated zone
3. Groundwater velocity
   a) Slow
   b) Fast

| Criteria | $MnO_4$ | $S_2O_8$ | Fenton's | $SO_4\bullet$ | Ozone |
|---|---|---|---|---|---|
| 1 | E | E | G | G | G |
| 2 | P/G | P/G | P/G | P/G | G |
| 3a | G | G | P | P | P |
| 3b | G | G | G | G | G |

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# Geochemical Considerations

1. Carbonate system (free radical scavengers)
2. High dissolved metals (precipitation issues)
3. High % organic matter ($f_{oc}$, DOC, etc.)

| Criteria | $MnO_4$ | $S_2O_8$ | Fenton's | $SO_4\bullet$ | Ozone |
|---|---|---|---|---|---|
| 1 | E | E | P | G | P |
| 2 | P | E | E | E | P |
| 3 | P | E | P | G | P |

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# Additional Considerations

| Criteria | $MnO_4$ | $S_2O_8$ | Fenton's | $SO_4\bullet$ | Ozone |
|---|---|---|---|---|---|
| Gas Production | Low | Low | High | Low | High |
| Heat Production | Low | Low | High | Low | Low |
| Fugitive Emissions | Low | Low | High | Low | High |
| Availability | E | E | E | E | G |
| Ease of Handling | G | E | G | E | G |
| Impact to Water Quality | Mod. | Mod. | Low | Mod. | Low |
| Patent Restrictions | Low | High | High | High | High |
| Technology Development | G | P | E | P | G |
| Available Information | G | P | G | P | G |
| Tried Field Applications | G | P | G | P | G |

P – poor   G – good   E – excellent   Mod. – Moderate

# Laboratory Treatability Studies



# Objectives

- **Determine the ability and rate of an oxidant to destroy the target contaminants**
- **Determine the oxidant demand of the site soils**
- **Determine the by-product formation of the oxidation-reduction reactions**
- **Analyze potential for metals release**
- **Determine catalyst requirements**

# Soil Oxidant Demand Tests

- **Often simple batch studies**
- **Soil added to known concentration of oxidant**
- **Consumption of oxidant monitored over time**
- **Variables**
  - **Time**
  - **Oxidant concentration**
  - **Catalyst concentration**
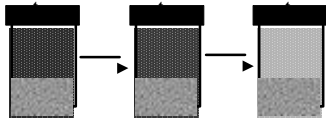


# Soil Oxidant Demand Tests

- **Soil demand has been shown to vary considerably between soils**
- **Can very <1 g/kg to >10 g/kg**
- **Factors affecting SOD**
  - **Organic matter**
  - **Reduced metals**
  - **Minerals**
  - **Applied oxidant concentration**
- **Post treatment metals can also be analyzed to determine if mobilization has occurred**

# Contaminant Treatability Tests

- **Often simple batch studies**
- **Contaminant added to known concentration of oxidant**
- **Contaminant Concentration Monitored overtime**
- **Can be run with/without soils**
- **Variables**
  - **Time**
  - **Contaminant concentration**
  - **Catalyst concentration**
  - **Reactant concentration**
  - **By-product concentration**



VS
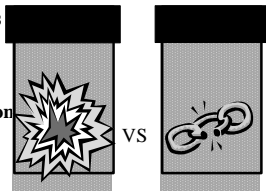
# Column Studies

- **Better simulate subsurface conditions**
- **Variables**
  - **Time**
  - **Contaminant concentration**
  - **Catalyst concentration**
  - **Reactant concentration**
  - **By-Product concentration**
- **More Expensive**
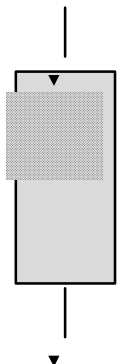
## Additional Considerations

- **Batch studies assume complete mixing**

- **May underestimate surface reactions**

- **Doesn't simulate subsurface conditions and discrete chemistry (mixing fronts etc.)**

- **Concentration dependent**

**1**
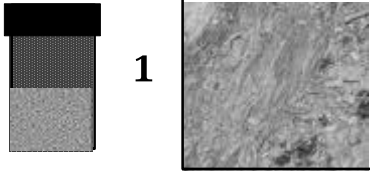
## Field Pilot Tests

## Pilot Test Objectives

- **Evaluate efficacy of selected oxidant to degrade target compounds**
- **Evaluate oxidants affect on aquifer**
  - **Hydraulic conductivity**
  - **Geochemistry – pH, redox**
  - **Mobilization of naturally occurring chromium**
- **Determine full-scale design parameters**
  - **Oxidant loading**
  - **Injection well spacing**
  - **Injection pressures and flow rates**

## Expectations

- **How do we measure success?**

- **Pilot test typically will not accomplish remediation clean-up goals**

- **Contaminant rebound will likely occur in groundwater**
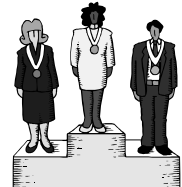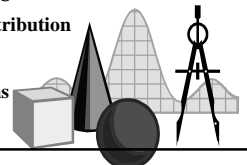
## Design Considerations

- **Range from simple push-pull test to elaborate multi-point injection/monitoring studies**

- **Must account for contaminant, geology, chemistry, hydrogeology**

- **Regulatory considerations**
  - **Water quality effects**
  - **Off-site migration control**

**OR**

- **Budget**

**Pilot study design determined by goals of each study.**

## Design Considerations

- **Duration**
  - **Must be based on site conditions**
  - **Reaction kinetics**
  - **Typically days to weeks**
- **Oxidant Loading**
  - **Need sufficient oxidant mass to affect measurable reduction in COC**
  - **SOD, contaminant mass, distribution**
- **Location**
  - **Representative site conditions**
  - **Worst case conditions**

## Design Considerations
### Monitoring

- **Based on rates of**
  - **Migration**
  - **Oxidant consumption**
  - **Contaminant destruction**
- **Regulatory issues**
  - **Intermediate formation**
  - **Migration**
  - **Water quality exceedences (directly or indirectly)**

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## Design Considerations
### Monitoring

| Typical Groundwater Parameters | |
|---|---|
| **Parameter** | **Method** |
| Contaminants | Varies – EPA 8260, 8270 |
| Oxidant | Field test kit |
| Metals | EPA Method 200.7 (ICP), SM 3120B |
| Major Cations | EPA Method 200.7 (ICP), SM 3120B |
| Anions | EPA Method 310.1, SM 2320B |
| Alkalinity | EPA Method 310.1, SM 2320B |
| ORP (EH) | Field Measurement |
| pH | Field Measurement |
| Temp | Field Measurement |
| Conductivity | Field Measurement |

Adapted From ITRC Technical/Regulatory Guidelines for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2001

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## Design Considerations
### Monitoring

- **System Monitoring**
  - **Mass of oxidant**
  - **Mass of catalysts**
  - **Injection rates**
  - **Volumes**
  - **Pressures**
  - **Radius of influence**

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## Design Considerations
### Health and Safety

- **Oxidants are strong chemicals – very hazardous !!**
- **Avoid contact with skin**
- **Breathing hazard with dust or mist**
- **Compatibility should be checked\***
- **Gas production / fugitive emissions**

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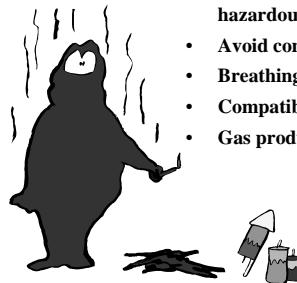
## Design Considerations
### Regulatory

- **Safe Drinking Water Act's (SDWA) Underground Injection Control (UIC)**
- **Injection wells are designated as Class V under UIC and need variance or permit by rule**
- **Variances becoming more common and accepted**
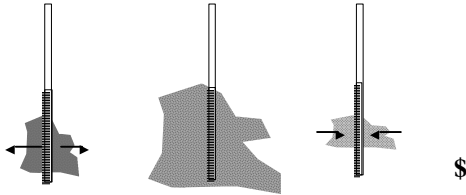- **May require permitting (RCRA) where above ground treatment, storage, or disposal occurs**

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## Approaches

- **Site specific, depends on**
  - **Geology**
  - **Contaminant**
  - **Oxidant**
- **Must consider project goals and budget**

## Single-Well Tests

- **Push-pull tests**
- **Inject known volume of oxidant and conservative tracer**
- **Extract and analyze change**
- **Compare to control test**

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## Single-Well Tests

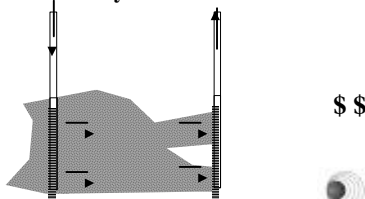| <u>Advantages</u> | <u>Disadvantages</u> |
|---|---|
| - **Minimal equipment needs**<br>- **Short duration (1 to 3 days)**<br>- **Low cost**<br>- **Use existing well***<br>- **Estimate of SOD**<br>- **Estimate of COC destruction**<br>- **Low volume of reagent used** | - **Provides limited information on full-scale delivery method**<br>- **Generates groundwater that may require disposal or treatment** |

## Dual Well Tests

- **Injection / extraction tests (circulation tests)**
- **Inject known volume/mass of oxidant and conservative tracer**
- **Extract and analyze**

$ $

## Dual Well Tests

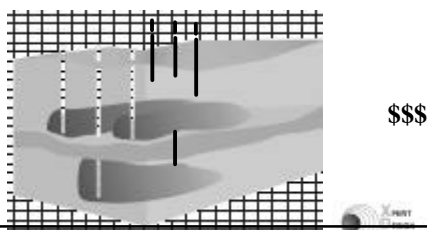| <u>Advantages</u> | <u>Disadvantages</u> |
|---|---|
| - **Larger aquifer volume tested**<br>- **Better estimation of SOD**<br>- **Better estimation of COC destruction**<br>- **Better estimate of oxidant distribution**<br>- **Low equipment needs** | - **Typically requires installation of injection points/wells**<br>- **May or may not be able to re-inject extracted water**<br>- **Permitting for re-injection of extracted water**<br>- **Longer duration (1 to 2 weeks)** |

## Multi-Well Tests

- **Multi-point injection**
- **Inject known volume/mass of oxidant**
- **Monitor multiple points over time**

$$$

## Multi-Well Tests

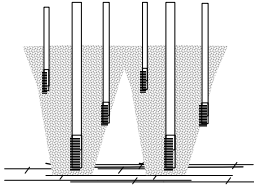| <u>Advantages</u> | <u>Disadvantages</u> |
|---|---|
| - **Applicable to all oxidants**<br>- **Enables better ROI determination**<br>- **Able to better simulate full-scale application** | - **High cost ($$$)**<br>- **Requires installation of multiple wells**<br>- **Longer duration**<br>- **Higher oxidant batching/injection equip needs** |

## Sparge Tests

- **Inject known volume/mass of oxidant gas**
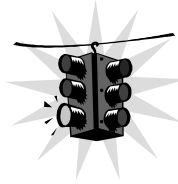- **Monitor fugitive gas**

**$$**

## Sparge Tests

| Advantages | Disadvantages |
|---|---|
| • Good approximation of full-scale application<br>• Well established technique | • Moderate Cost ($$)<br>• May require vadose monitoring or SVE<br>• High Equipment needs |

## Limitations

- **Short duration**
  - **Mass transfer limitations**
  - **Limited oxidant loading**
- **Small treatment area**
  - **Variable geology**
  - **Variable contaminant distribution**
- **Limited monitoring**
  - **Can miss reactions – timing is important**
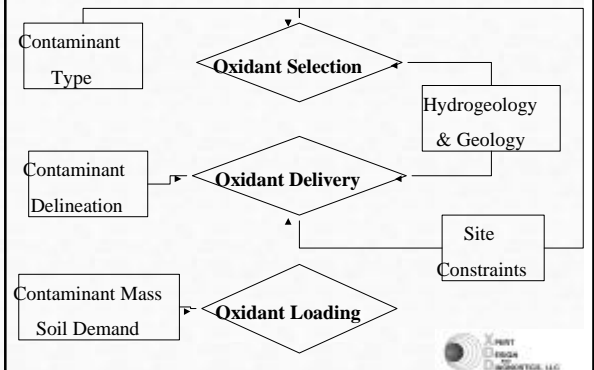- **Cost too often dictates SOW!**

## *Thank You!*
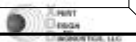
## Full-Scale Application

*"Matching the oxidant and in situ delivery system to the contaminants of concern and the site conditions is key"*

## Full-Scale Conceptual Design

Contaminant Type → Oxidant Selection ← Hydrogeology & Geology

Contaminant Delineation → Oxidant Delivery ← Site Constraints

Contaminant Mass Soil Demand → Oxidant Loading

## Design Factors

- **Primarily a source zone technology**

- **May be cost prohibitive for use on large diffuse plumes**

- **Most oxidants stimulate bioremediation**

- **Mass transfer limitations**

## ISCO & Bioremediation

- **Microbial communities can temporarily be altered but usually bounce back quickly**

- **Often beneficial (post-oxidant injection)**

  - **Ozone, hydrogen peroxide provide oxygen that can stimulate aerobic biodegradation**

  - **Increased bioavailability of organic carbon can stimulate biodegradation (aerobic & anaerobic)**

  - **Increases contaminant bioavailability**

## Mass Transfer Limitations

- **ISCO reaction kinetics vs. contaminant desorption and diffusion processes**

- **Contaminant rebound often observed after "batch" oxidant applications**

- **May necessitate multiple applications or a phased approach**

Source: Pignatello and Xing (1996)

## Oxidant Stability

- **Stability/persistence/presence of oxidant in the subsurface will provide for treatment over prolonged period of time**

- **Order of oxidant persistence**

  - **Permanganate > Persulfate > Hydrogen Peroxide > Ozone**

## Methods of Oxidant Injection

- **Sands**
  - **Direct Push**
  - **Conventional Injection Wells**
  - **Pressure Pulse Injection**
- **Clays**
  - **Large Diameter Augers**
  - **Electrokinetic's**
- **Bedrock**
  - **Surface Infiltration**
  - **Hydraulic Fracturing & Emplacement**
  - **Pneumatic Fracturing & Injection**

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## Overburden Applications
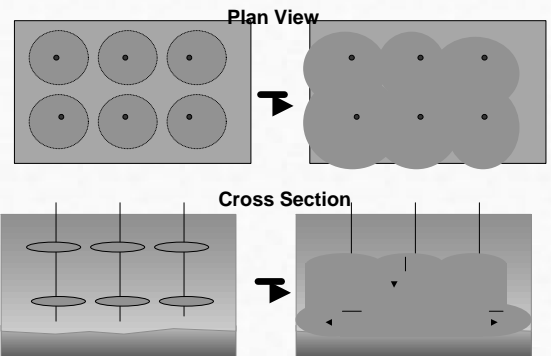


10' – 20'

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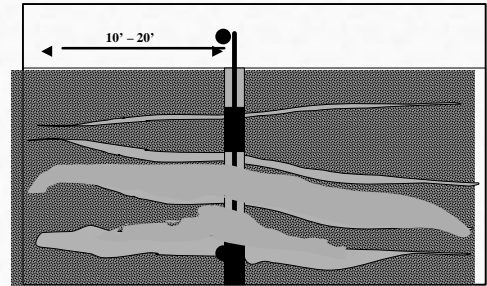
## Direct Push

- **Injection through drilling rods**
- **Temporary or fixed injection points**
- **Used in an array typically 10 to 20 feet on center**
- **Flexible delivery method, can customize injection intervals**
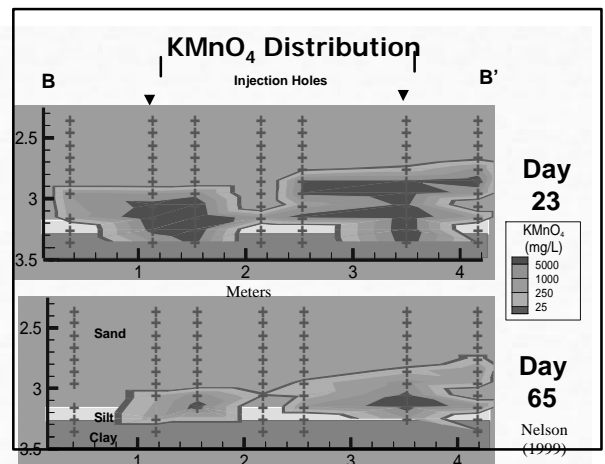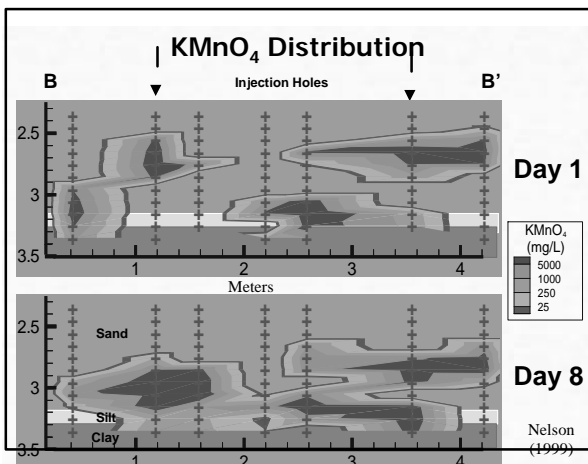- **Limited by installation depth**
- **Moderate cost**

Source: University of Waterloo, Canada

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## Conceptual Approach - Coalescing Discs

**Plan View**

**Cross Section**



Nelson (1999)

---

## KMnO$_4$ Distribution

**B**          Injection Holes          **B'**

**Day 1**

KMnO$_4$ (mg/L)
5000
1000
250
25

Meters

Sand

**Day 8**

Silt
Clay

Nelson (1999)

---

## KMnO$_4$ Distribution

**B**          Injection Holes          **B'**

**Day 23**

KMnO$_4$ (mg/L)
5000
1000
250
25

Meters

Sand

**Day 65**

Silt
Clay

Nelson (1999)

## Conventional Injection Wells

- **Standard well construction**
- **Low pressure injection (0 to 30 psi)**
- **Used in an array or transects**
- **Relies on groundwater/density advection and dispersion for distribution**
- **Oxidant distribution limited by screen placement and soil heterogeneity**

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## DUOX Application (Persulfate/Permanganate)

- Active Manufacturing facility
- Water bearing strata: gravely-sand, semi-confined, 8-10 ft thick, 5 ft/day velocity
- Residual DNAPL in silt lenses at an aquitard interface
- Main contaminants: TCE, cis-DCE, VC
- Generally reducing groundwater conditions (ORP: 0 to –150 mV)

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## DUOX Injection Well Layout



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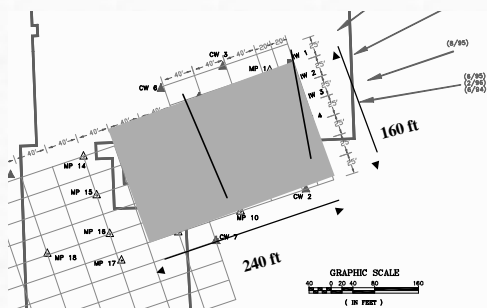
## DUOX Batching System

- **Fully Automated**
- **Minimized Oxidant Handling**
- **Persulfate ~ 8,200 kg (2 months)**
- **KMnO4 ~ 45,000 kg (6 months)**



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## DUOX Summary

- **> 3,000 kg TCE DNAPL destroyed due to**
  - **Direct oxidation by persulfate/permanganate**
  - **Enhanced anaerobic bioremediation**
- **Monitored Natural Attenuation currently being evaluated for remaining dissolved TCE plume**

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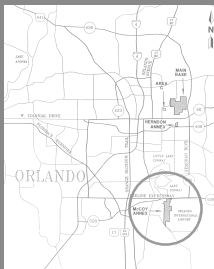## Fenton's Reagent In-Situ Chemical Oxidation of TCE Source Area NTC Orlando, Florida

Steve Tsangaris – CH2M Hill Constructors, Inc.
Barbara Nwokike – SOUTHDIV NAVFAC
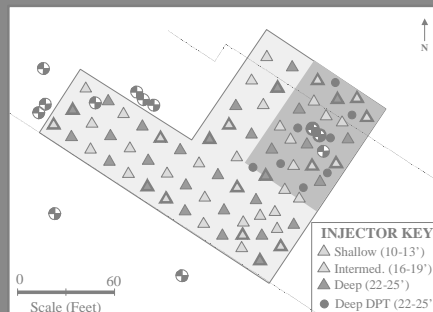Dan Bryant – Geo-Cleanse International, Inc.

**CH2MHILL**

## Study Area 17



- NTC Orlando operationally closed under BRAC (1999).
- Former Motor Pool area.
- Buildings at SA 17 used for general storage, USTs.
- Initial site investigations began in 1995.
- Past remedial actions included 185-yd$^3$ excavation of PAH-contaminated soil.

## Phase I Injector Installation & Sampling Locations



INJECTOR KEY
△ Shallow (10-13')
△ Intermed. (16-19')
▲ Deep (22-25')
● Deep DPT (22-25')

Scale (Feet)    0    60
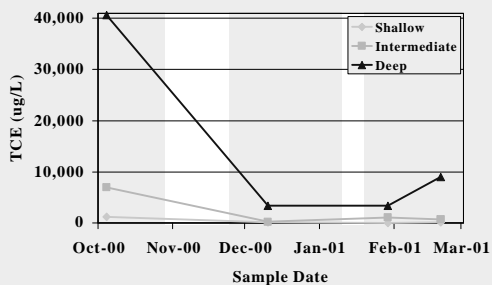
## Study Area 17



## Field Injection



- 2 Mobilizations
  - Nov. 7 – Nov. 30, 2000
  - Jan. 15 – Jan. 18, 2001
- 21 Days of Treatment
- 77 Injectors in 3 levels
- 6,307 Gallons of Hydrogen Peroxide

## Injection Results
### TCE Zonal Averages



## SA 17 Treatment Summary

- Phase I - Completed 21 days of injection.
  - 6,307 gallons of hydrogen peroxide
  - 77 injectors
- Achieved remedial objective in shallow zone (no significant rebound after 2 months).
- Significant reductions in intermediate and deep zone with associated chloride production.
- Additional delineation in progress (deeper than 31 feet below grade) for Phase II treatment.

# Ozone Case Study

- **Former manufactured gas plant (MGP)**
- **Site under an elevated roadway interchange**
- **Tar, oils, and lamp back**
  - **PAHs ~ 2,500 mg/kg**
  - **TPH ~ 28,000 mg/kg**
- **Treatment target 1 mg/kg BaP for soil**

IT Corporation

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## Ozone Case Study - System Schematic
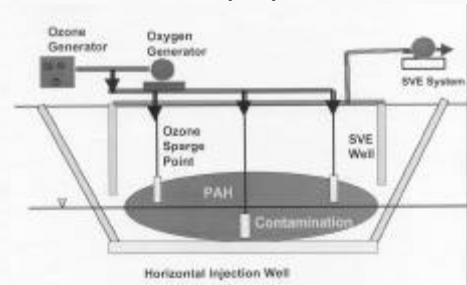


1. **Oxidation of PAH and TPH**
2. **Enhanced bioremediation through oxygen enrichment**
3. **Vapor collection**

IT Corporation

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# Ozone Case Study
# Vertical Sparging Points



**33 Points Installed to 25 ft**

IT Corporation

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# Ozone Case Study
# Horizontal Well Installation



- **Total length: 360 ft**
- **Screen length: 135 ft**
- **Install 6 feet below water table**
- **Install through center of plume**

IT Corporation

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# Ozone Case Study



**Oxygen Generation Trailer**
- **Molecular sieve – ambient air**
- **95% $O_2$ at 100 psi**

**Ozone Generation Trailer**
- **50 lb/day capacity**
- **5% $O_3$ at 15 psi & 7 scfm**

IT Corporation

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# Ozone Case Study Results

- Free Product
  - Free product appeared after 4 months of operation
  - Decreasing overall percentage of heavy hydrocarbons (C13-C34)
  - Increase of lighter chains (C5-C10)
- Groundwater
  - Contaminant concentrations at or below detection limits by third quarter
- Soil
  - Target contaminants below detection limit by fourth quarter
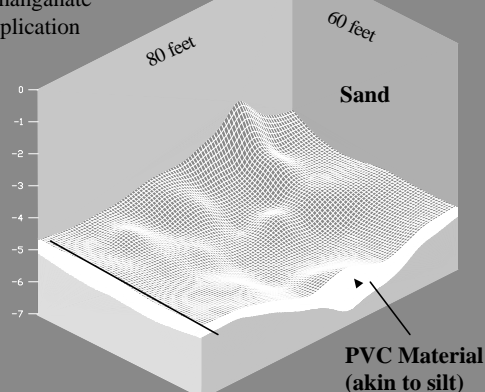- Site Closure for Industrial Risk Achieved

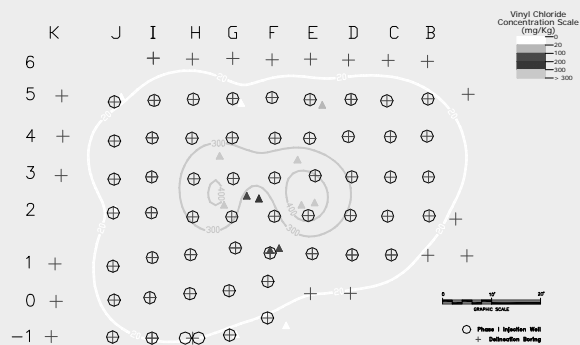IT Corporation

## Applications in Silts/Clays

- Oxidant Stability Key
- Pin-Cushion Approach
- Large Diameter Auger
- Electrokinetic's

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Sodium Permanganate Application

80 feet
60 feet

**Sand**

0
-1
-2
-3
-4
-5
-6
-7

**PVC Material (akin to silt)**

---

## Injection Well Layout



Vinyl Chloride Concentration Scale (mg/Kg)
20
100
200
300
> 300

K  J  I  H  G  F  E  D  C  B

6
5
4
3
2
1
0
-1

○ Phase I Injection Well
+ Delineation Boring
▲ Soil Boring (Color Based On Concentration)

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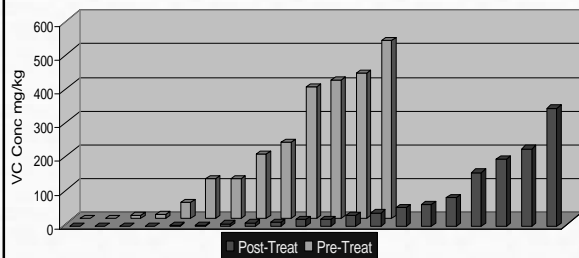## Portable Oxidant Delivery (POD) System

- **Two injection events (20 days total)**
- **55 injection points at 8 ft spacing**
- **Simultaneous multi-point injection**
- **4,000 lbs NaMnO$_4$**
- **Fully self-contained**

Source: XDD, LLC

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### Soil VC Concentrations Pre-Treat vs. Post-Treat



VC Conc mg/kg

600
500
400
300
200
100
0

■ Post-Treat  ■ Pre-Treat

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## Sodium Permanganate – Silts/Clays: Results

- Distribution of oxidant non-uniform due to low permeability and heterogeneity
- VC concentrations reduced to below or near cleanup goal (20 mg/kg) in 70% of post-treatment soil samples
- VC mass destruction ~ 62%
- Progressive decline in soil VOC concentration observed over 3 month period
- No further action required for soils
- MNA for dissolved plume

## Large Diameter Augers

- **3 to 10 foot diameter augers equipped with injection nozzles**

- **Equipment developed for installing grout/cement pilings**

- **Uniform soil/oxidant mixing**

- **Limited by installation depth, subsurface utilities and structures**

- **High cost**



Source: Office of Science and Technology (OST) Deep Soil Mixing ID:52   http://tms.em.doe.gov/
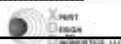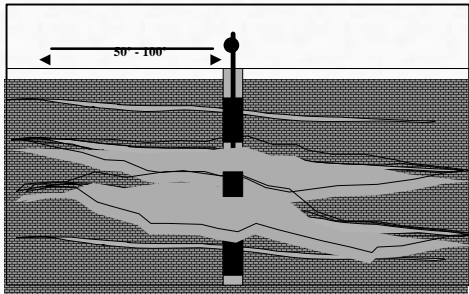
## Electrokinetic Migration in Clay

- Kaolin Clay ~ 37% moisture content
- $KMnO_4$
- 20 volts, 6 mA
- Current increases with $KMnO_4$ coverage
- Applicable to persulfate
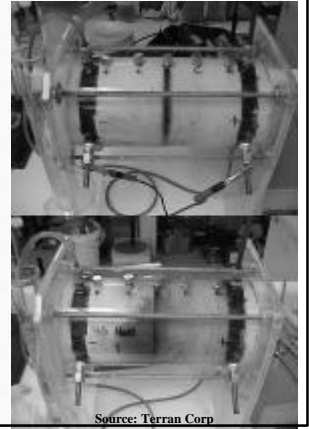


Source: Terran Corp

## Bedrock Applications



50' - 100'

## Surface Infiltration

- **Superfund Site in Maine**
- **Vertically Fractured Rock**
- **PCE DNAPL to 110 ft**
- **Overburden (2 to 4 ft) Removed**
- **Vadose Zone ~ 30 ft**
- **Pilot Test ~ 300 kg $KMnO_4$**
- **150 ft ROI**
- **GW [PCE] 30 mg/L to < 1 mg/L**
- **Rebound observed**



## Hydraulic Fracturing

- **High pressure liquid injection to propagate fracture network**
- **Emplacement of sand or solid oxidant into fractures**
- **Injection of oxidants through sand filled fractures**
- **Applicable to low permeable formations/ bedrock**
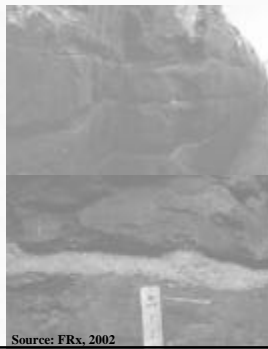


Source: FRx, 2002

## Pneumatic Fracturing/Injection

- **High pressure nitrogen gas injection to propagate fracture network**
- **Liquid oxidant injection through fracture network**
- **Applicable to low permeable formations/bedrock**



Source: XDD, LLC

## Pneumatic Fracturing/Injection



Source: XDD, LLC

- PCE/TCE DNAPL in clay 5 - 10 ft bgs
- Injection pressure = 100 psi
- Gas flow rate = 2000 scfm
- Oxidant flow rate = 50 gpm
- 95% reduction
- Non-uniform distribution

Liquid sodium permanganate is more hazardous to handle than solid potassium permanganate, but easier to batch.

*Thank You!*

# In-Situ Chemical Oxidation of MTBE

By Kara L. Kelley, Michael C. Marley and Kenneth L. Sperry

In-situ chemical oxidation (ISCO) can be a cost-effective method for the destruction of source areas of methyl tertiary butyl ether (MTBE). Several ISCO processes have been tested successfully under laboratory conditions and a few have proven successful when field tested for the destruction of MTBE. This article reviews the state of the art with respect to MTBE oxidation for several common oxidants and Advanced Oxidation Processes (AOPs). AOPs are oxidants or oxidant combinations characterized by the production of the hydroxyl radical (OH•). This drastically increases the oxidative capabilities of the ISCO system (Liang et al., 2001, Mitani et al., 2001, and Acero et al., 2001). Four frequently used oxidants are reviewed in this article: hydrogen peroxide ($H_2O_2$), ozone ($O_3$), permanganate ($MnO_4$-), and persulfate ($S_2O_8^{2-}$).

## Choosing an Oxidant

When choosing an oxidant for a specific remediation strategy, trade-offs exist between oxidant strength and stability in the subsurface. Typically, the more aggressive oxidants are less stable, have shorter half-lives and prove more difficult to transport in the subsurface (Clayton et al., 2000, Cookson et al., unpublished). A measure of oxidant strength, the standard oxidation-reduction potential ($E°$) is the electromotive force in units of volts (V) of the oxidation/reduction reaction. Larger, positive $E°$ values indicate a greater potential for the half reaction to proceed as written. Table 1 lists the $E°$ values and half cell reactions for the oxidants reviewed in this article.

When implementing an ISCO process, several water quality parameters may influence the initiation and the effectiveness of the reaction. These parameters include pH, alkalinity, natural organic matter and the concentration of interfering compounds (Acero et al. 2001). Soil oxidant demand (SOD) from natural soil organics, inorganics and co-contaminants can significantly increase the amount of oxidant required to treat the target contaminant (Parikh et al. 2001).

Oxidation end products are an important consideration in the selection of an oxidant, as not all oxidants have proven successful in complete mineralization of MTBE. Tert-butyl formate (TBF) and tert-butyl alcohol (TBA) are the major intermediate products in the oxidative reactions of MTBE. It has been postulated that because TBF and TBA may be partially oxidized during the oxidation of MTBE, that these intermediates may be more susceptible to biological degradation and therefore subject to natural attenuation (Leetham, 2001, Mitani et al., 2001). End products of complete mineralization of MTBE include carbon dioxide and water (Wagler and Malley, 1994). Other factors, including regulatory restrictions, need to be considered when choosing an oxidant for a specific application. ISCO has gained regulatory acceptance, thereby facilitating permitting issues associated with ISCO implementation (Oberle and Schroder, 2000).

A matrix of important features of the oxidants discussed in this article is presented in Table 1. The matrix includes MTBE/oxidant reactions tested, oxidant to MTBE weight ratios and half cell reactions for the oxidants. The matrix also lists information about the oxidants such as the formation of the hydroxyl radical, if the oxidant is more effective at a particular pH range, the electromotive force of each oxidant and whether the oxidant has been used in a successful field application.

For an oxidant that has specific pH requirements, pre-treatment of the aquifer with an acid solution to lower the pH is typically considered, although acidic conditions can be hard to maintain depending on the buffering capacity of the soil. Experience has shown that aquifer pre-treatment can be costly and ineffective (Leetham, 2001, Nyer and Vance, 1999, Oberle and Schroder, 2000, Yeh and Novak, 1995). Other options are available for reducing the requirement of a low pH such as injecting hydrogen peroxide with a chelated catalyst promoting radical formation at a higher pH (i.e., 6 pH units) (Kakarla, 2002).

## Description of ISCO Processes

Typically an oxidant is injected into the subsurface in solution. Other methods of delivery include sparging or emplacing the oxidant as a solid into the subsurface (e.g., permanganate solid has been used in place of sand as a propant in hydraulic fracturing). Once the oxidant contacts organics in situ, a reaction occurs where electrons removed from the oxidant are gained by the organic, producing a typically harmless end product having either a higher oxygen or lower hydrogen content than the original compound (Suthersan, 1997). Each of the four oxi-

dants discussed in this article reacts differently in the subsurface, and it is important to consider the unique qualities of each reaction when choosing an oxidant.

## Reactions of the ISCO Processes

### Hydrogen Peroxide

Oxidants in the subsurface react via specific mechanisms unique to the chemical used. For example, when a concentrated $H_2O_2$ solution (e.g., 35 to 50%, by weight) is injected into the subsurface, it promotes volatilization. The resulting violent decomposition of the $H_2O_2$ solution produces heat, a high volume of $O_2$ and $CO_2$ gases and possibly salts from non-hydrocarbon constituents. The heat and high volume gas production causes localized volatilization of susceptible contaminants. To promote radical oxidation, less concentrated solutions of $H_2O_2$ (e.g., 12% by weight) are injected with a stabilizer to slow the decomposition of $H_2O_2$, and an acidified iron salt or chelated form of ferrous iron (a Fenton's or Fenton's type reaction) to promote OH• formation (Kakarla, 2002). Incomplete degradation of MTBE was observed by some of the authors researched. By products of the reaction included TBF, TBA and acetone (Burbano et al., 2001, Yeh and Novak, 1995)

### Ozone

Depending upon the application method, MTBE oxidation may occur in gas-phase bubbles via the Creigee mechanism or in the aqueous phase via direct $O_3$ or OH• oxidation. Direct ozonation is the reaction of compounds with molecular $O_3$, and indirect ozonation involves the reaction of compounds with the OH• produced during $O_3$ decay. The direct oxidation of MTBE via $O_3$ is slower than oxidation via the OH• with rate constants for the hydroxyl radical reaction typically nine orders of magnitude faster than the rate constants for $O_3$ alone (Acero et al., 2001, Liang et al., 2001, Mitani et al., 2001, Vel Leitner 1994). The application of $O_3$ in conjunction with other oxidants such as $H_2O_2$ (an AOP called Peroxone), or a process that combines $O_3$ with air stripping, may provide efficient oxidation of MTBE via the OH• or volatilization. Using these processes, it is typically difficult to determine the mechanism of oxidation. Incomplete oxidation of MTBE was noted by several authors with by products of the reaction including TBF, TBA, formaldehyde, 2-methoxy-2-methyl propionaldehyde, acetone, methyl acetate and hydroxyisobutyraldehyde (Acero et al. 2001, Liang et al., 2001, Mitani et al., 2001, Vel Leitner 1994).

### Matrix of Oxidants, Reactions with MTBE ($C_5H_{12}O$) and Considerations for Use in the Field

| Oxidant & Reaction with MTBE | Oxidant/ MTBE (lb/lb) | OH· | Optimal pH | EO[2] (V) | Field Tested |
|---|---|---|---|---|---|
| $H_2O_2$<br>$C_5H_{12}O + 15H_2O_2$ $^{(Fe)}$→<br>$5CO_2 + 21H_2O$ [1] | 5.8/1 | ✓ | 3 - 5 | 1.78 | ✓ |
| $O_3$ | NA[3] | ✓ | [4] | 2.07 | ✓ |
| $MnO_4^-$<br>$21 MnO_4^- + 2 C_5H_{12}O →$<br>$21MnO_2 + 10 CO_2 + 24 OH^-$ | 2.8/1 | | [5] | 1.70 | ✓ |
| $S_2O_8^{2-}$ | NA[3] | ✓ | 2.5-11 | 2.01[6] |  |

(1) Stoichiometric equation for MTBE and $H_2O_2$ in the presence of ferrous iron, optimal pH shown for Fentons Reaction

(2) Referenced from Huang et al., unpublished
Half cell reactions for EO values:
$O_{3(g)} + 2H^+ + 2e^- → O_{2(g)} + H_2O$
$S_2O_8^{2-} + 2e^- → 2SO_4^{2-}$
$H_2O_2 + 2H^+ + 2e^- → 2H_2O$
$MnO_4^- + 4H^+ + 3e^- → MnO_{2(s)} + 2H_2O$

(3) NA, information not available

(4) If used with $H_2O_2$ or Fentons reagent 3 to 5 pH units otherwise increasing pH leads to faster ozone decomposition

(5) Three electrons are exchanged at a pH range of 3.5 to 12

(6) Catalyzed persulfate EO is 2.6

### Table 1

### Permanganate

Groundwater pH affects the kinetics of the permanganate reaction, and determines whether the oxidation will involve one, three or five electron exchanges (Damm et al., unpublished). However, most aquifers have a pH within the 3.5 to 12 pH unit range, it can be expected that three electrons will be exchanged during in situ oxidation. TBA is the end product of the permanganate/MTBE reaction as shown in the theoretical chemical equation: 2 $MnO_4^- + 1 C_5H_{12}O → 2 MnO_2 + C_4H_{10}O + 1 CO_2 + 2 OH^-$ (Damm et al., unpublished).

### Persulfate

Sodium persulfate ($N_2S_2O_8$) is a radical-based ($SO_4^-$• and/or OH•) oxidant. Huang et al., unpublished, found that parameters that increase activation energy of the persulfate/MTBE reaction (24.5 ± 1.6 kcal/mol) include temperature, persulfate concentration, pH and ionic strength. However, it was determined that increasing pH over the range of 2.5-11 and ionic strength over the range of 0.11-0.53 M decreased the reaction rate. In addition, it was determined that persulfate oxidation is ineffective for the oxidation of MTBE at atmospheric pressure and ambient temperature (i.e., uncatalyzed) or in the absence of transition metal ions. However, heat-assisted persulfate oxida-

tion completely oxidized MTBE and intermediates TBF, TBA, acetone and methyl acetate (Huang et al., unpublished).

## Proven Effectiveness in Field or Laboratory

Hydrogen peroxide, ozone and permanganate have been used in field applications specifically for the oxidation of MTBE. No known field application exists for persulfate but a successful catalyzed persulfate oxidation of MTBE in the laboratory has been completed. All of the oxidants discussed in this article have proven successful for ISCO applications for VOCs and contaminants other than MTBE. The field and laboratory experience for each oxidant is discussed below.

## Hydrogen Peroxide

Yeh and Novak in 1995 conducted a batch laboratory study of the degradation of MTBE using $H_2O_2$ with and without an iron catalyst. They found that the MTBE concentration did not decrease in a solution of $H_2O_2$ and distilled water. When ferrous iron was added to the solution, oxidation of MTBE was rapid. Although sufficient iron was available to initially catalyze the oxidation of MTBE, the iron was quickly oxidized to $Fe^{3+}$, which was no longer capable of catalyzing the formation of Fenton's reagent. The authors found that MTBE was chemically oxidized to TBA and acetone and that the oxidation was influenced primarily by $H_2O_2$ concentration and pH. It was determined from the study that at a pH at which iron hydroxides and oxides will form, evident by the presence of a brown colored solution, degradation of MTBE will stop. In the studies, more MTBE was oxidized at a pH of 4.0 as compared to a pH of 6.5. Hydrogen peroxide favors acidic conditions and the optimum pH for Fenton's reaction is between a pH of 2 to 3 (Yeh and Novak, 1995).

## Ozone

A variety of batch experiments were conducted comparing MTBE oxidation with $O_3$ and $O_3$ in conjunction with $H_2O_2$. With the addition of $O_3$ to a $H_2O_2$ solution, the OH• was determined to be the predominant reactant (Acero et al., 2001, Liang et al., 2001, Vel Leitner 1994).

A pilot study using ozone was conducted at a gasoline service station on Long Island, N.Y. A plume containing BTEX and MTBE had contaminated an aquifer volume of over 17,000,000 ft³. The MTBE plume had spread to 2,400 feet downgradient from the site. Two Spargepoints® ($O_3$/air) were installed at different depths, both in the saturated zone, in a single borehole. Ozone and air were injected for four weeks. The radius of influence for the system was estimated to be twenty eight feet. Initial MTBE concentrations were 45 ppb and 6,300 ppb. After seven weeks of groundwater monitoring, MTBE concentrations had dropped to 2 ppb and 79 ppb resulting in reductions of 96% and 99% in two monitoring wells located twelve and twenty eight feet downgradient of the injection well, respectively. The oxidation mechanism for this pilot test was not stated nor was volatilization elimi-

nated as a possible mechanism of the reaction (Nichols and Voci, 2001).

## Permanganate

Damm et al., (unpublished) performed batch tests using permanganate to oxidize MTBE. The author found that the effects of pH were minimal, which is common in $KMnO_4$ reaction kinetics under typical groundwater conditions (Parikh et al. 2001). While the batch study showed that oxidation of MTBE was favored under more acidic or alkaline conditions than under neutral conditions, the change in reaction rate was so small that a pH adjustment of the aquifer before permanganate treatment would be unnecessary. The rate of MTBE oxidation via the permanganate ion was $1.4 \times 10^{-6}$ mg $L^{-1}$ $h^{-1}$. Complete oxidation of MTBE did not occur. Intermediate and end products included TBF and TBA, and the measured molar consumption of permanganate and MTBE was 2:1, (permanganate:MTBE) (Damm et al., unpublished). Clayton et al., (2000), in a multi-site field evaluation of ISCO, concluded that MTBE could be successfully oxidized to TBA with permanganate. Treatment efficiencies of >99% were reported for both low-level dissolved and high-level dissolved/sorbed MTBE (Clayton et al., 2000).

## Persulfate

Sodium persulfate was used in batch studies for MTBE oxidation performed by Huang et al., unpublished. Rate constants for the concentrated (8 g/L) solution at a pH of 7, ionic strength of 0.11M, in a phosphate-buffered solution range from 0.13 - 5.8 x $10^{-4}$s$^{-1}$ as the temperature was increased from 20 to 50° C. In a persulfate solution at 40° C, four MTBE oxidation intermediate products TBF, TBA, methyl acetate and acetone were also readily oxidized (Huang et al., unpublished). For in-situ applications, radical based oxidation can occur under heat or metal catalyzed reactions (Bruell et al., 2001, Sperry et al., 2001) .

## Practical Design Considerations

## Hydrogen Peroxide

When using hydrogen peroxide to create a Fenton's type reaction (if an insufficient amount of naturally occurring ferrous iron exists in the target aquifer), the reaction can be catalyzed by the addition of ferrous sulfate ($FeSO_4$) in the treatment solution. An acid solution may be used to reduce the pH of the soil matrix if needed, and a buffer (e.g., phosphate, especially monophosphate) solution may help to stabilize $H_2O_2$ in the subsurface (Kealy et al., 2001, Yeh and Novak, 1995). Yeh and Novak (1995) suggest that the presence of phosphate provided stabilization of the $H_2O_2$ and did not inhibit the chemical oxidation of MTBE.

Health and safety issues relating to ISCO using $H_2O_2$ are significant. There is more than one undocumented story concerning the application or mis-application of highly concentrated $H_2O_2$ and liquid amendments. The oxidation reaction is exothermic and is capable of producing

extreme heat and $H_2O_2$ concentrations as low as 11% can cause groundwater to boil (Oberle and Schroder, 2000). Experienced persons should handle, mix and inject a concentrated $H_2O_2$ solution into the subsurface.

## Ozone

Ozone sparged into the subsurface may have a limited radius of influence. Ozone typically dissociates rapidly resulting in limited transportation in the subsurface. A consideration when using ozone for ISCO is the formation of bromate. Bromate is a chemical that is formed during the ozonation of natural waters where bromide is present. In environments with a high bromide content, such as seawater, bromide concentrations are approximately 65 mg/L (Acero et al., 2001, Chang and Yen, 2000, Liang et al., 2001, West Hertfordshire Health Authority, 2001). The EPA has set the maximum contaminant level for bromate at 0.010 ppm because toxicology studies have shown bromate to be carcinogenic in laboratory animals (USEPA 815-F-98-010, 1998).

## Permanganate

Permanganate has stability and persistence in the subsurface. Permanganate has a longer half-life in the subsurface compared to more powerful oxidants including $O_3$ or $H_2O_2$. Oxidation induced pH changes that occur in the subsurface during ISCO using permanganate can mobilize hexavalent chromium. Immobile $Cr^{+3}$ is oxidized to mobile $Cr^{+6}$. Hexavalent chromium naturally attenuates and $Cr^{+6}$ levels return to background over time and as groundwater conditions return to pretreatment pH levels. One estimate of the half-life of dissolved chromium is six days (Clayton et al., 2000). The permanganate ion oxidizes MTBE less rapidly (by 2-3 orders of magnitude) than other advanced oxidizing agents (Damm et al., unpublished).

## Persulfate

Persulfate may be a good candidate for MTBE oxidation under catalyzed conditions, given its high solubility and stability in normal subsurface conditions, and its complete mineralization of MTBE in the laboratory (Huang et al., unpublished).

## Conclusions

ISCO is likely not a good candidate for large dilute MTBE plumes or as a barrier system. ISCO is more effective as a source area remediation tool. Before choosing an ISCO process site, hydrological, geological, and geochemical conditions combined with knowledge of the particular contaminant(s) of concern must be known and evaluated in order to choose the appropriate oxidant and method of delivery. A laboratory treatability study followed by a field pilot test provide invaluable data as to how the oxidant and delivery system will perform at a specific site, and to aid in the design of the full scale ISCO system. Properly designed ISCO is an effective alternative to biodegradation, pump and treat or soil vapor extrac-

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